Effects of Temperature and Moisture on Dilute-Acid Steam Explosion Pretreatment of Corn Stover and Cellulase Enzyme Digestibility

Melvin P. Tucker, Kyoung H. Kim, Mildred M. Newman,
and Quang A. Nguyen

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Abstract

Corn stover is emerging as a viable feedstock for production of bioethanol from renewable resources. Solubilization of hemicellulosic sugars and enhancement in cellulose digestibility occurs during pretreatment of corn stover feedstock. In this study, dilute sulfuric acid pretreatment of corn stover was performed in a steam explosion reactor at 160°C, 180°C and 190°C, approximately 1 wt-% H_2SO_4, and 70 s to 150 s residence times. The combined severity (Log Ro-pH), an expression relating pH, temperature and residence time of pretreatment, ranged from 1.85 to 2.4. Soluble xylose yields varied from 63% to 77% of theoretical from pretreatments of corn stover at 160°C and 180°C. However, yields greater than 90% of theoretical were found with dilute-acid pretreatments at 190° C. A marked increase in xylose yield was found by increasing pretreatment temperatures from 180°C to 190°C at similar combined severities. Increasing moisture content from 55 wt-% to 63 wt-% (47 wt-% to 37 wt-% dry solids) resulted in a narrower range of higher combined severities required for high xylose solubilization. Simultaneous saccharification and fermentation (SSF) of washed solids from corn stover pretreated at 190°C, using an enzyme loading of 15 FPU/g cellulose, gave ethanol yields in excess of 85%. Similar SSF ethanol yields were found using washed solid residues from 160°C and 180°C pretreatments at similar combined severities using a higher enzyme loading of 26.5 FPU/g cellulose.

Introduction

- Dilute Acid pretreatment can improve the accessibility of cellulase enzymes to cellulose in lignocellulosic feedstocks.
- Dilute acid pretreatment of corn stover has been shown to solubilize as much as 90% of the xylan under pretreatment temperatures ranging from 140° to 180°C (*1,2*).
- In general, higher pretreatment temperatures and shorter reactor residence times result in higher soluble xylose recovery yields and enzymatic digestibility (*3*).
- Pretreatment at 190°C improves both soluble xylose recovery yields and cellulase enzyme digestibility.

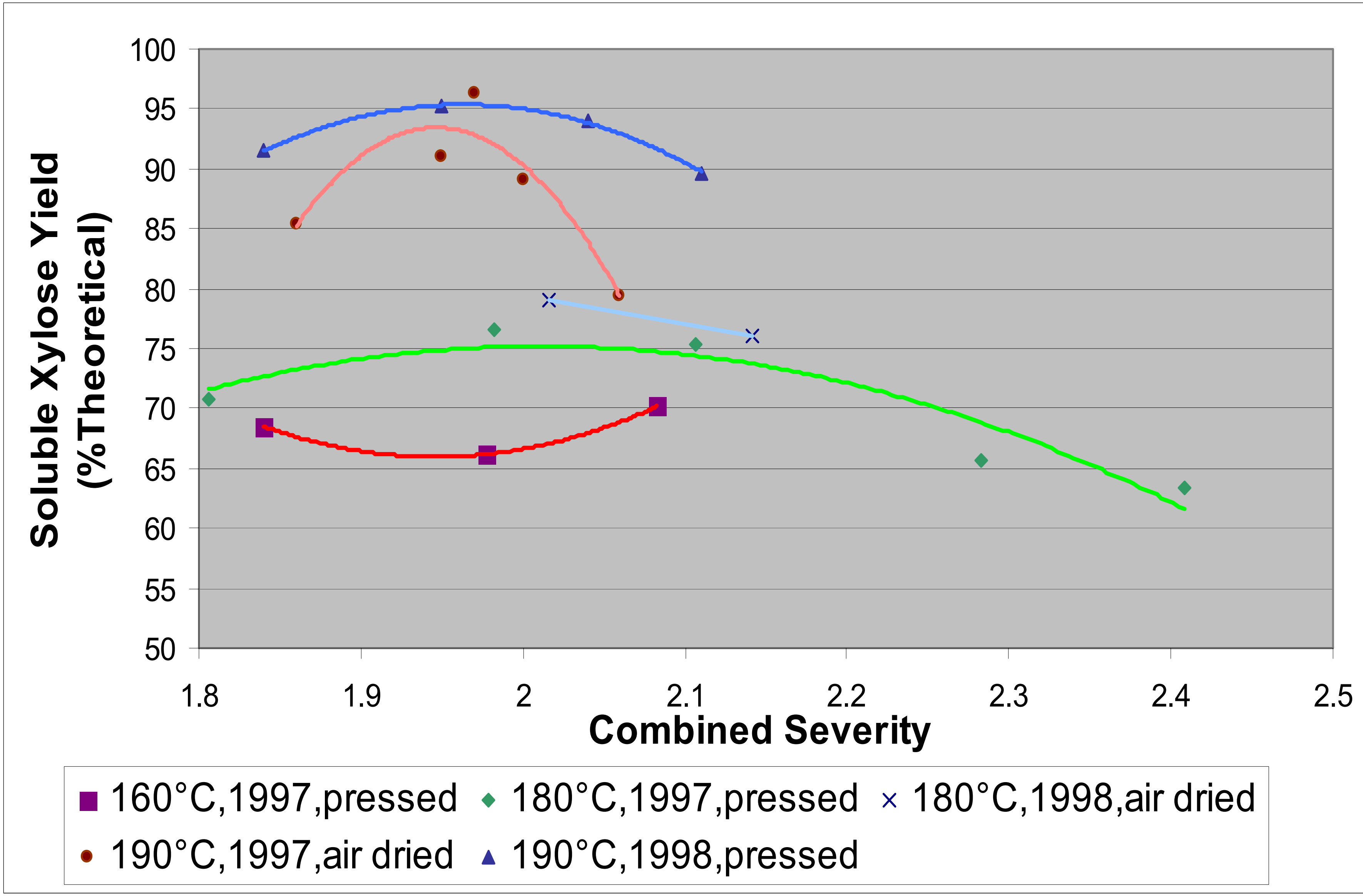

Figure 1. Total soluble xylose yields from dilute-acid catalyzed steam explosion pretreatment of corn stover at various temperatures, combine severities, harvest years, and dewatering methods.

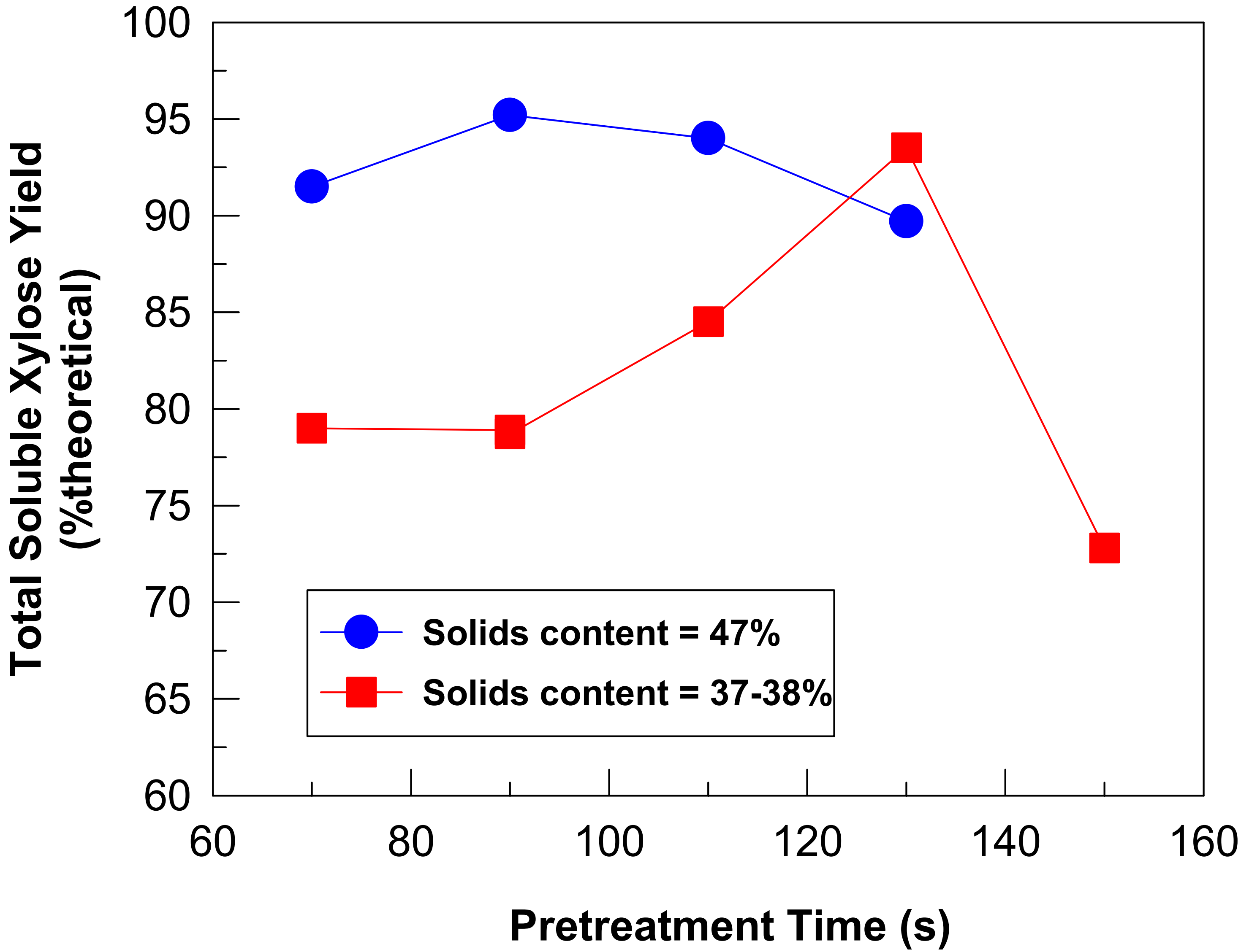

Figure 2. Effects of moisture level in acid impregnated corn stover feedstocks on pretreatments at 190°C. The closed red squares show soluble xylose yields from pretreatments using acid impregnated feedstock pressed to 37-38 wt-% solids content. The closed blue circles show soluble xylose yields from acid impregnated feedstocks pressed to 47 wt-% solids content.

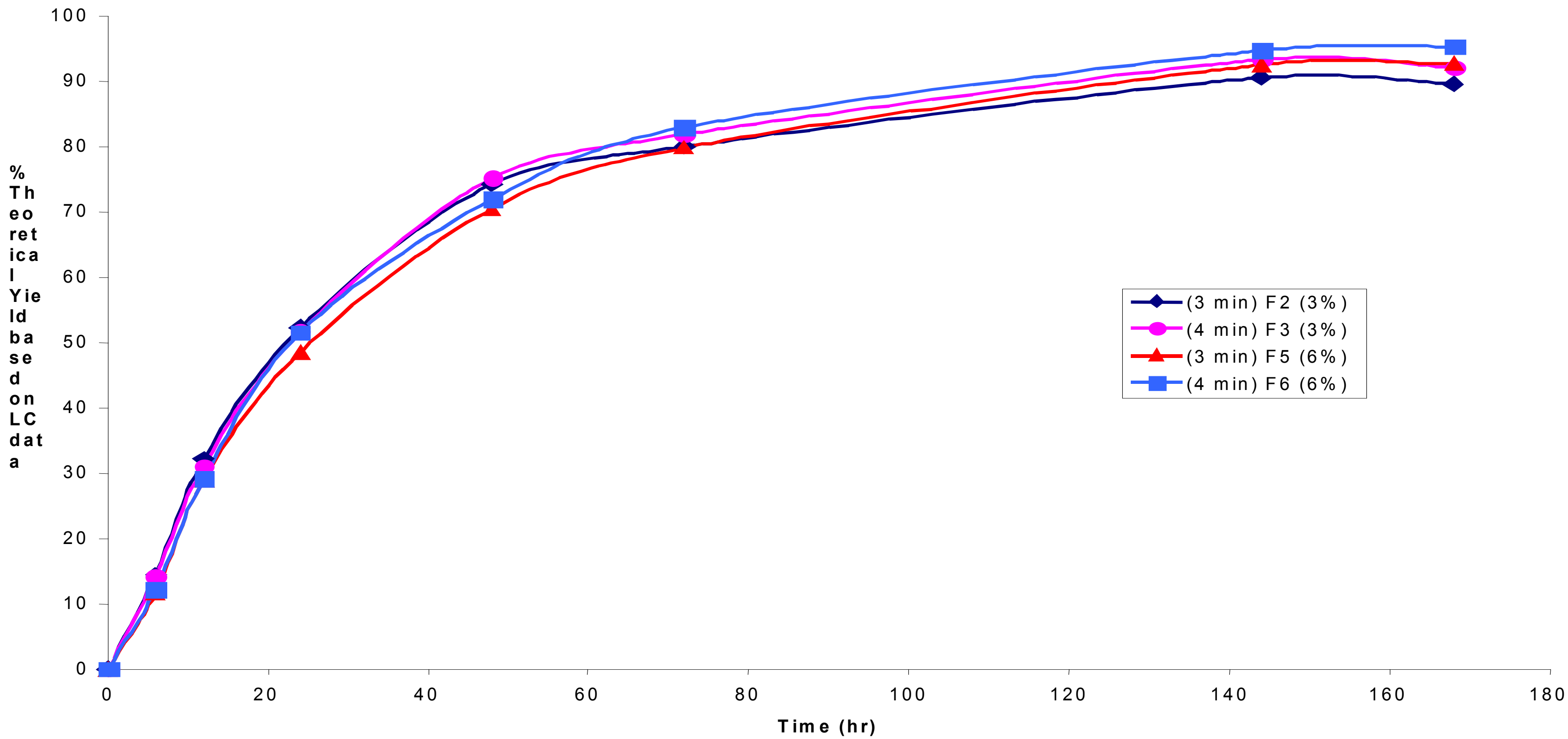

Figure 3. Effects of cellulose loading on initial rates and final extent of reaction of converting cellulose to ethanol. Pretreatment of corn stover was carried out at 180°C for 3 and 4 min with 1.1% H_2SO_4. The assays were carried out at 32°C, with an enzyme loading of 26.5 FPU/g CPN cellulase enzyme, and a solids loading giving final cellulose content of 2.8% or 5.6%. The initial enzyme and cellulose loadings (25 FPU/g and 3.0 wt-% or 6 wt-% cellulose) were adjusted based on predictions using an NIR method. The enzyme and cellulose loadings were later corrected to the values presented in this figure once wet chemical analysis data became available.

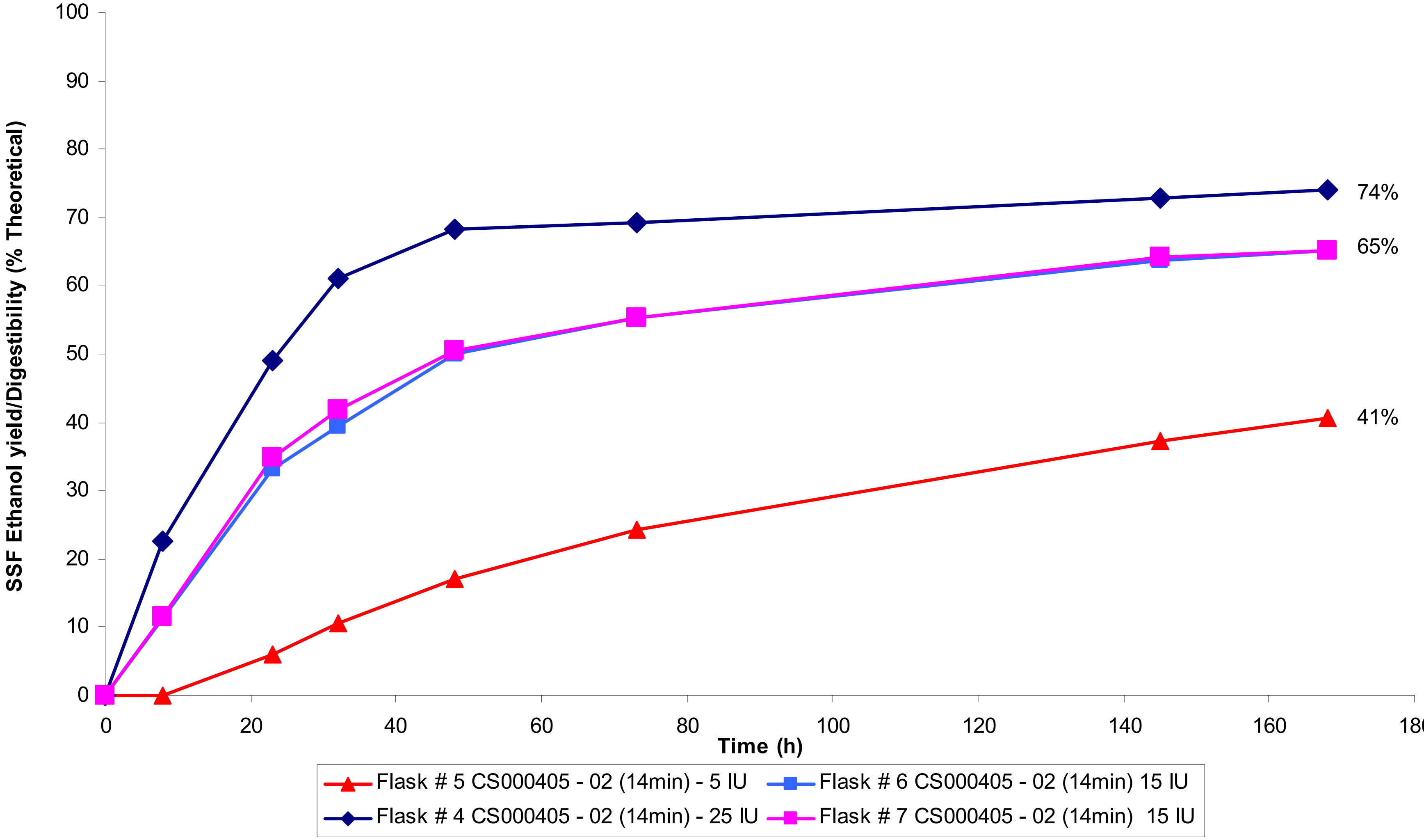

Figure 4. Effects of enzyme loading on initial rates and final extent of reaction of converting cellulose to ethanol. Pretreatment of corn stover was carried out at 160°C for 14 min with 1.07% H_2SO_4. The assays were carried out at 32°C, with enzyme loadings of 5, 15, and 25 FPU/g cellulose. The enzyme was CPN cellulase enzyme, and a solids loading giving a final cellulose content of 6% cellulose based upon wet chemical analysis of the 160°C pretreated residue.

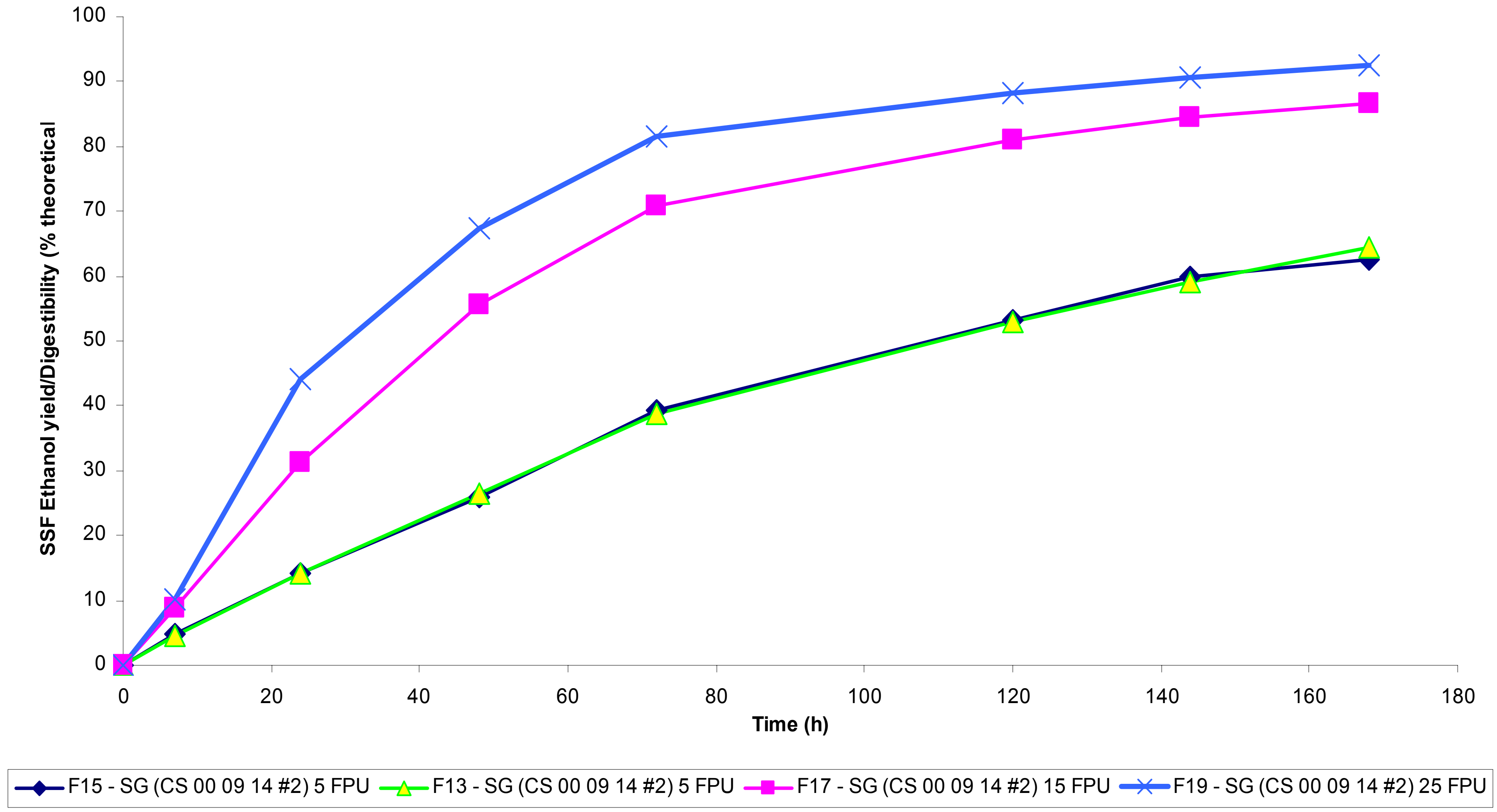

Figure 5. Effects of enzyme loading on initial rates and final extent of reaction of converting cellulose to ethanol. Pretreatment of corn stover was carried out at 190°C for 90 s with 1.06% H_2SO_4. The assays were carried out at 32°C, with enzyme loadings of 5, 15, and 25 FPU/g cellulose. The enzyme was CPN cellulase enzyme, and a solids loading giving a final cellulose content of 6% cellulose based upon wet chemical analysis of the 190°C pretreated residue.

Table 1. Summary of corn stover pretreatments

Run #	Input feedstock				Pretreatment conditions			After pretreatment		
	Harvest year	Dewatering method	Solids content (wt%)	Acid conc. (%, w/w)	Temp. (°C)	Time (s)	Combined severity	Solids content (wt%)	pH of liquor	Total soluble xylose yield (%theoretical)
1	1997	Pressing	50	1.07	160	480	1.84	38.3	1.37	68.5
2	1997	Pressing	50	1.07	160	660	1.98	36.5	1.44	66.2
3	1997	Pressing	50	1.07	160	840	2.08	35.7	1.49	70.2
4	1997	Pressing	50	1.07	180	120	1.81	27.1	1.56	70.8
5	1997	Pressing	50	1.07	180	180	1.98	37.4	1.87	76.5
6	1997	Pressing	50	1.07	180	240	2.11	36.6	1.90	75.4
7	1997	Pressing	50	1.07	180	360	2.28	32.9	1.93	65.6
8	1997	Pressing	50	1.07	180	480	2.41	33.0	1.95	63.3
9	1997	Drying	46	1.06	190	70	1.86	25.2	1.1	85.4
10	1997	Drying	46	1.06	190	85	1.95	26.9	1.1	92.9
11	1997	Drying	46	1.06	190	90	1.97	25.5	1.0	96.3
12	1997	Drying	46	1.06	190	95	2.00	25.5	1.1	89.1
13	1997	Drying	46	1.06	190	110	2.06	27.6	1.0	79.4
14	1998	Pressing	47	1.0	190	70	1.84	26.9	1.2	91.5
15	1998	Pressing	47	1.0	190	90	1.95	29.1	1.3	95.2
16	1998	Pressing	47	1.0	190	110	2.04	27.1	1.3	94.0
17	1998	Pressing	47	1.0	190	130	2.11	25.5	1.4	89.7
18	1998	Pressing	38	1.0	190	70	1.86	18.4	1.3	79.0
19	1998	Pressing	38	1.0	190	90	1.97	20.8	1.1	78.9
20	1998	Pressing	38	1.0	190	90	1.97	25.3	1.0	78.7
21	1998	Pressing	38	1.0	190	110	2.05	23.6	1.1	84.5
22	1998	Pressing	37	1.0	190	130	2.13	22.3	1.2	93.5
23	1998	Pressing	37	1.0	190	150	2.09	29.2	1.1	72.8

Table 2. Summary of sugar recovery and degradation product yields

Run #		Glucose	Xylose	Galactose	Arabinose	Mannose	Acetic acid	HMF	Furfural
1	% recovery	6.4	68.5	70.7	54.6	>100	37.5		
	g/100 g feedstock	2.84	17.26	1.58	1.97	1.41	0.64	0.04	1.79
	% monomers*	70.6	93.9	90.7	90.6	74.7			
2	% recovery	6.5	66.2	69.5	52.1	>100	43.3		
	g/100 g feedstock	2.90	16.68	1.56	1.88	1.426.7	0.74	0.05	3.03
	% monomers*	75.4	91.0	92.1	88.2	78.1			
3	% recovery	6.7	70.2	63.5	48.3	>100	49.0		
	g/100 g feedstock	2.95	17.69	98.2	91.6	1.28	0.84	0.07	3.57
	% monomers*	74.3	81.6	1.42	1.74	87.2			
4	% recovery	7.2	70.8	69.3	54.5	>100	34.6		
	g/100 g feedstock	3.18	17.84	1.55	1.96	1.49	0.6	0.05	2.26
	% monomers*	100	94.1	100	100	100			
5	% recovery	6.8	76.5	74.7	60.5	>100	55.8		
	g/100 g feedstock	3.00	19.27	1.67	2.18	1.25	0.96	0.06	3.85
	% monomers*	87.2	98.4	92.8	100	94.9			
6	% recovery	7.6	75.4	75.5	58.6	>100	59.6		
	g/100 g feedstock	3.36	19.01	1.69	2.11	1.27	1.03	0.06	4.82
	% monomers*	86.4	96.3	92.1	99.0	97.4			
7	% recovery	7.8	65.6	71.3	53.4	>100	64.4		
	g/100 g feedstock	3.46	16.52	1.60	1.92	1.31	1.11	0.12	7.02
	% monomers*	91.3	98.1	94.3	100	100			
8	% recovery	8.2	63.3	69.9	51.8	>100	71.7		
	g/100 g feedstock	3.64	15.96	1.57	1.87	1.33	1.24	0.14	8.03
	% monomers*	92.9	99.4	94.6	100	100			
9	% recovery	6.1	85.4	92.1	72.0	124.1	56.5		
	g/100 g feedstock	2.70	21.52	2.06	2.59	0.46	0.98	0.03	0.51
	% monomers*	85.2	83.8	78.2	83.0	100.0			
10	% recovery	6.7	91.0	91.0	66.6	87.7	53.5		
	g/100 g feedstock	2.99	22.93	2.04	2.40	0.32	0.93	0.03	0.49
	% monomers*	100.0	84.2	70.5	88.0	98.3			
11	% recovery	8.1	96.3	99.3	81.0	121.0	63.8		
	g/100 g feedstock	3.61	24.27	2.22	2.91	0.45	1.10	0.03	0.66
	% monomers*	100.0	86.9	73.6	81.1	91.8			
12	% recovery	6.6	89.1	111.3	70.6	99.9	69.2		
	g/100 g feedstock	2.93	22.46	2.49	2.54	0.37	1.20	0.05	0.72
	% monomers*	100.0	85.2	68.2	81.3	84.9			
13	% recovery	5.6	79.4	85.2	68.5	163.8	70.1		
	g/100 g feedstock	2.50	20.00	1.91	2.47	0.61	1.21	0.06	0.62
	% monomers*	75.5	78.0	59.2	77.9	42.0			

Materials and Methods

- Corn stover was harvested during two different years by Biomass AgriProducts (B/MAP) from Harlan, Iowa area. Following collection, the stover was washed in NREL PDU Wash Tank, drained and partially air-dried (~45 wt-%).
- Washed and partially dried corn stover was acid impregnated with ~ 1 wt-% H_2SO_4 prior to pressing in hydraulic press, or ~ 0.36 wt-% prior to partially air-drying (30°C to 40°C) to ~1 wt-% final acid concentration. Acid loading was ~ 1.2 g H_2SO_4/100 g biomass (dry).
- Acid impregnated feedstock was pretreated in NREL Digester (steam explosion reactor) at 160°C, 180°C, and 190°C for various residence times.
- Pretreated slurries were collected in "bags" in a cooled flash tank connected to the NREL Digester.
- Pretreated slurries were pressed in NREL's hydraulic press to obtain liquor for analysis of sugars, organic acids, and volatiles using HPLC, and pressed solids.
- Pressed pretreated solids were washed exhaustively with hot water for wet chemical solids analysis and NIR characterization.
- Washed solids were subjected to SSF assays to determine digestibility. Washed solids at ~3 wt-% and ~6 wt-% cellulose loading, were digested with cellulase enzyme at 5, 15, and 25 FPU/g cellulose, and fermented in the presence of *S. cerevisiae* D_5A yeast at 32°C. Cellulose digestibility is reported in terms of ethanol yield from theoretical glucan to glucose conversion.

Results and Discussion

- Maximum soluble xylose recovery yields favor higher temperatures and shorter residence times due to first-order kinetics of xylan hydrolysis and xylose degradation reactions (Figure 1).
- Acid catalyzed steam explosion pretreatment of corn stover at 190° gave higher soluble xylose yields in the slurry liquors and higher cellulase enzyme digestibility of the solid residues than pretreatments at 160°C or 180°C (Figures 3-5).
- Temperatures higher than 190°C may require too short of reactor residence times for achieving uniform heating of the heterogenous corn stover particles. Non-uniform heating within the reactor will result in lower soluble xylose yields.
- Corn stalks contain approximately 28% nodes which have higher density and lignin content (20% lignin in nodes compared to 16.7% in whole stocks, 14.6% in leaves and 13.3% in pith) (4). This requires higher temperatures to achieve sufficient breakdown of the lignin-carbohydrate complex resulting in higher soluble xylose yields.

Results and Discussion (cont.)

- The differences in soluble xylose yields between different harvest years were minimal (see Figure 1).
- The differences in soluble xylose yields between different methods of dewatering the acid impregnated corn stover feedstocks were minimal (see Figure 1).
- Moisture level in the acid impregnated feedstock had a large impact on the combined severity for maximum xylose yield of pretreatment of corn stover at 190°C (see Figure 2). The lower the moisture content (higher solids) in the acid impregnated feedstock, the broader the curve for pretreatment. The drier acid impregnated feedstocks are more amenable to pretreatments in a large scale reactor where controlling conditions in the reactor is more difficult. The drier acid impregnated feedstock would decrease the scale of downstream processing equipment and lime neutralization needed in a large scale process.

Conclusions

- Acid catalyzed steam explosion pretreatment of corn stover (pre-impregnated with ~1% sulfuric acid) at 190°C for about 90 seconds gave >90% total soluble xylose yields and >90% SSF cellulase enzyme digestibilities.
- The conditions explored, and the results presented in this study were utilized to guide pretreatment experiments at the pilot scale using both the NREL PDU vertical and horizontal Sunds Hydrolyzer pretreatment reactors.

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